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Separation of Alkalies in Boiler Water Analysis

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A Method for the Separation of the Alkalies in Boiler Water Analysis

..BY..

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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The estimation of the alkalies and especially their separation from Calcium and magnesium is one of the most important in the realm of chemical analysis. The necessity of accurately determining the amounts of sodium and potassium in clays, soils, cements, boiler waters etc, substances extensively used and of the utmost technical importance, has called forth much work in this branch of the subject. Many methods have been brought forward from time to time, some excellent, others not so good, and some of the oldest still find a widespread application. The very existence, however, of so many methods perhaps shows that, in general, no particular method has found complete or extensive favor.

Although the determinations in this case have been made altogether with reference to boiler waters, the method would be the same with the other classes of similar substances and hence no distinction will be made in the discussion of previous work.

The majority of the methods proposed are direct; in fact only two important indirect methods were found. There is a further fact noticeable in a review of these methods and that is that so many of them form a group in which the underlying principle of the separation is to obtain the magnesium, sodium and potassium in the form of carbonates.

The first method proposed was published by Fr. Sonnenschein in 1848.(1) He takes a mixture of the chlorides of sodium, potassium and magnesium and, after evaporation to dryness, gently heats them to expel ammonia salts. The dry mass is then boiled with water and silver carbonate is added to strong alkalinity. The magnesium is hereby precipitated as carbonate and the silver remains on the filter as chloride. The alkalies may be determined in the filtrate, while the magnesium may be estimated in the usual manner as phosphate by first dissolving it from the mixed precipitate with hydrochloric acid.

In 1850 Ebelmen(2,3,4) published a method

which in reality was simply a modification of Berzelius' method which was the first process proposed by anyone and the then prevailing one. Berzelius dissolved the sulphates of the three metals in water and treated the solution with an excess of Barium acetate, by which means the sulphates were changed to acetates. After filtation and evaporation to dryness of the filtrate, the mass is heated to redness to change the bases to carbonates. By the addition of hot water the sodium and potassium carbonates dissolve while barium and magnesium remain insoluble. The latter may now be easily separated from the former and determined in the usual manner. Ebelmen makes the criticism that the process is long and tiresome and that the barium sulphate formed is slow in filtering and comes through the filter even after boiling. The alkaline carbonates are also found to contain some sulphates, which is of great detriment in the use of platinic chloride.

Ebelmen used, instead of barium acetate, barium carbonate

and a current of carbon dioxide. This change shortened the process but did not do away with the difficulty of the barium sulphate. The maximum error found in his method was a loss of 2 o/o on the final product when the process was carried out as directed but rose when the carbon dioxide was not passed in or when ammonium carbonate was used. In spite of its comparative accuracy the method is still too long and clumsy to find a ready acceptance.

In 1852 Deville (5+6) proposed the following method. He separated the calcium and barium from the other three alkalies by means of ammonium oxalate, then evaporated the filtrate and expelled the ammonium salts by heating. Water was then added together with an excess of oxalic acid. After again evaporating the dish was heated to redness, thus changing the oxalates to carbonates. The magnesium carbonate being insoluble in water, may easily be separated from the soluble sodium and potassium carbonates. The method seems to be a

good one and is recommended(7+8) by Smith, who has used it extensively. It must be mentioned however that it is only applicable with nitrates and chlorides but not with sulphates. Some traces of the chlorine are usually found in the final residue.

Deville's statements concerning the oxalic acid method for the purification of the alkalies were also confirmed by G. Lewinstein(9) in 1856. Many other contributors speak of it with favor and it seems to have attained a great degree of popularity because of its simplicity and brevity.

In 1858 H. Wurtz(10) used a variation of the method but lost rather than gained by the change. He treated the combined chlorides with nitric acid and, after evaporation, heated the residue strongly in a platinum dish. One bad point, as the author states, comes in here for some of the platinum is always oxidized. The substance was then melted up with ammonium carbonate and after the addition of water more carbon dioxide had to be passed in to complete the precipitation.

In 1873 Th. Scheerer(11) published a method

which, as far as could be seen, was identical with those of Deville and Lewinstein, mentioned above. He, however, makes the criticism that the method is totally inapplicable in the case of sulphates.

In 1852 C. von Hauer introduced a somewhat strange method; one which would not gain ready acceptance because of the slowness of the process and because of other obvious difficulties. The magnesium is separated from the sodium and potassium by precipitation with ammonium arsenate. To the precipitate obtained the author gives the following formula, of course in the old style nomenclature: $MgO, NH_4O - As_2O_5 - + HO$. By this the author probably meant magnesium ammonium arsenate. The filtrate must be acidified with sulphuric formic or acetic acids and hydrogen sulphide passed in to take out the arsenic. The chief objections here would be in regard to the passing in of the H_2S. This would probably have to be repeated several times to make sure of the complete removal of the arsenic and further the precipitate would probably be hard to filter and slow to wash.

Heintz (1848)(13) describes a method in which he precipitates out magnesium from an ammoniacal solution of the three chlorides with phosphoric acid. The excess of the latter reagent in the filtrate is taken out with a solution of lead nitrate or lead acetate. The excess of lead salt may be taken out with ammonium carbonate and ammonia, the alkalies being determined as usual in the filtrate. This method somewhat resembles in form, the one I have under consideration, but it has the drawback that an undesirable third acid is added to the solution in the shape of the lead compound.

In 1859 Scheerer(14) used a method in which he determined the combined weights of the three salts as sulphates. He then divided the solution of them into three parts and in one determined magnesium as the phosphate. In another part he determined the potassium with platinic chloride. It would seem that the magnesium would interfere here, but according to the author this is not the case. The sodium may be estimated by difference. as far as I can see there would be one

insurmountable objection here in the process as stated. The potassium compound must be in the shape of a chloride before complete precipitation of K_2PtCl_6 can occur. The remedy would be to bring them down as chlorides in the first place. Scheerer claims however that the method is accurate within .5 o/o of the final product.

G. Chancel (15) contributed an article in 1860 in which he described a method for separating magnesium from the alkalies by precipitating out the former as usual with ammonium phosphate in the presence of ammonia and ammonium chloride. The filtrate is then evaporated to dryness and heated till all ammonium salts are expelled. The residue is then dissolved in water and treated with silver nitrate and silver carbonate. Silver phosphate is thus precipitated; the excess of silver may be taken out with hydrochloric acid, the purified alkalies then remaining in the filtrate as chlorides.

In 1865 C. Ruber (16) published a modification of Scheerer's method (1859.) The same objection however holds here as before. After first determining the weight of the total sulphates,

He dissolves them but instead of dividing into three parts he precipitates the potassium with platinic chloride immediately. The excess of the reagent is taken out with ammonium chloride and in the filtrate the magnesium is determined as phosphate, the sodium being estimated by difference.

In 1887 F. A. Gooch (17) described a method by which he can separate the alkalies as chlorides from lithium, magnesium and calcium by the use of amyl alcohol. The principle of the process lies in the dehydrating power of the alcohol and also in its appropriate solvent action. When a mixture of the chlorides of magnesium, sodium and potassium are heated with the alcohol, water is gradually expelled and the sodium and potassium chloride are precipitated while the magnesium chloride remains in solution and may afterwards be thrown down. The amyl alcohol gives rise to very noxious fumes, which must be avoided. The error in this process never rose above 3.2 o/o on the final product but in the separation from the calcium it sometimes rose as high as 21 o/.

The first indirect method for the separation was proposed by K. List(18) in 1851. He brings the solution containing the three metals to dryness and heats in a platinum dish until all the ammonium salts, introduced at previous stages of the analysis, are expelled. Dilute sulphuric acid is then added and after re-evaporation they are once more heated, being now, naturally in the form of sulphates. The residue is then dissolved in water and the sulphuric acid content is determined by means of barium chloride, the excess of which must then be taken out with sulphuric acid. The magnesium may now be determined as phosphate. The following formulae are derived by the author for the calculation of the sodium and potassium

Let mass of sulphates = A | $s' = SO_3$ united with m
Let amount of SO_3 found = S | $s = SO_3$ " with $K + Na$.
' Amount of MgO found = m | a = amount $K + Na$ sulphate

Then $a = A - (m + s')$ and $s = S - S'$

$$\text{Then } K = \frac{\dfrac{s \cdot NaO + s - a}{SO_3}}{\dfrac{NaO}{KO} - 1} \qquad Na = \frac{\dfrac{s \cdot KO + s}{SO_3} - a}{\dfrac{KO}{NaO}}$$

This would of course be Na_2O + K_2O.

From the figures given List's method does not appear to be particularly accurate. In the case of sodium and magnesium the error was over six % on the final product. The method has no particular brevity or quickness of manipulation to recommend it. This fact coupled with the long calculation would seriously hinder its adoption.

A. Phillips (1860)(19) takes the sulphates of the three metals and precipitates the magnesium as phosphate. The amount of SO_3 is then determined by means of barium chloride. From these data the amounts of sodium and potassium may be calculated by the same formula as in List's method. These indirect methods do not seem to be extensively used being chiefly employed in cases where the sodium and potassium must be separated, this not being necessary in boiler waters. Even where the separation is necessary the process of directly precipitating out the potassium with $PtCl_4$ is better. No new processes have been found since 1887.

The method of the separation of the alkalies from magnesia which is under investigation here rests essentially

upon the following processes: The magnesia is taken out as usual with ammonium acid phosphate. The excess of the latter reagent is taken out with a solution of manganese chloride and this in turn is precipitated out of the filtrate with hydrogen peroxide in ammoniacal solution. after a review of the literature upon two phases of this process, it will be discussed in detail.

The work upon the trimanganese phosphates is scanty for practically no investigations have been carried on in the last twenty years. The extent of the literature on the subject is indicated by the following references:

In 1848 Heintz(20). investigated the manganese phosphates, chiefly with reference to modes of production. On adding sodium phosphate to a solution of manganese sulphate he obtained the trimanganophosphate as a white non crystalline precipitate which was almost insoluble in water but soluble in acids.

In 1861 Debray(21) found, after a series of experiments on the production of phosphates and among these the trimangano, that if a solution of phosphoric acid and a solution of manganese carbonate are heated together to 70°C, the di mangano salt results. If the crystals are heated in water to 100°C, the trimangano phosphate is formed, but a lower phosphate is left in solution. If the manganese is in excess the phosphoric acid is precipitated in the form of the crystallized tribasic phosphate, on continued boiling. Debray also proved that no chloro phosphates were formed on the substitution of manganese chloride for the carbonate.

Erlenmeyer and Heinrich in 1877(22) found that the tribasic phosphate is produced by treating manganese sulphate with disodium hydrogen phosphate. They did not find that by heating the dimangano salt in water they could get the tri mangano phosphate, as Debray had stated. Treatment with cold water however produced the desired result.

Braun in 1868(23) found that the addition

of a manganese chloride solution to a di-sodium acid phosphate solution produced a white precipitate, which, heated to boiling changes from a flocculent state to a crystalline state and is now the tribasic phosphate with seven molecules of water. When the manganese chloride is added to an excess of microcosmic salt solution the silky crystalline precipitate of manganese ammonium phosphate is formed.

In 1887 Joly(24) published a series of articles upon the earthy phosphates, considering chiefly their heats of formation. He found that there were two distinct stages in the precipitation, a colloidal state and then a crystalline state. If the colloidal precipitate is in the presence of an alkaline chloride, as sodium chloride, a double chloride appears containing two parts of the earthy base to one of the alkali. Berthelot(25) confirms these results.

The following references will give the extent of previous study on manganese dioxide and methods of precipitation with hydrogen peroxide.

Wright and Menke in 1880(26) made many experiments on the dioxide, preparing it in many ways (not, however, by means of hydrogen peroxide.) and found that the product they obtained was always hydrated, but that the water content is not constant. It usually contains some potassium when made from potassium permanganate, or in the presence of KOH. In the presence of certain potassium salts the precipitate seems to decompose. When but little potassium is absorbed there seems to be a deficiency of oxygen, a condition also brought about by the hard heating of the solution.

The following separations of manganese from other metals by the use of hydrogen peroxide have been found. P. Jannasch and C. J. Franzek (1891)(27) separated manganese from nickel and cobalt by means of H_2O_2 but found that they were only successful in getting the manganese free when an alkali cyanide was present in the solution. E. Donat(28) and Ad. Carnot(29) had found previously the composition of the manganese precipitate corresponded to the formula $MnO \cdot 5MnO_2$. In 1894 Jannasch(30) and

Niederhofheim published a method for separating manganese from zinc by means of the peroxide. The precipitation must be brought about in the presence of potassium cyanide and potassium hydroxide. The authors state that some alkali is taken up but can be gotten rid of by means of reprecipitation. The next year Jannasch(31,32,33,34,35) made similar successful separations from silver and mercury. When he tried(36) the separation from copper he found that much copper was contained in the precipitate, but an increase in the amount of ammonia proved beneficial. The author mentions that he had much trouble in obtaining pure hydrogen peroxide.

In 1877 G. Rosenthal(37) made determinations of manganese with hydrogen peroxide and ammonia. The amounts he used of the latter were only slight but he obtained a precipitate that settled readily. He found that the precipitate, prepared either with bromine or hydrogen peroxide, readily took up BaO or ZnO.

The details of the method as carried out in these investigations are as follows:

The magnesia in the boiler water or soluble silicate is determined in the usual manner by precipitation, in an alkaline medium, with ammonium acid phosphate. The precipitate, after being allowed to settle over night, is filtered off, dried, burnt and weighed as the magnesium pyrophosphate. In the filtrate there should now be nothing but the alkalies and the excess of the phosphate reagent used. To eliminate the latter a sufficient amount of a rather dilute solution of manganese chloride is added. In these experiments 10cc of 10% solution were used. To carry out the precipitation here in the neatest manner the solution should be acid or neutral before the addition of the manganese chloride. The solution must then be neutralized or made slightly alkaline with ammonia. In order to get this point somewhat exactly, a few drops of rosolic acid

were used as indicator and an excess ammonia was thus avoided. Although the presence of ammonia here does no essential harm if not in too great an amount, it causes some manganese hydroxide to precipitate along with the manganese phosphate, which causes a waste of time in filtering and washing. Too much ammonia would, of course, prevent the precipitation of all of the phosphoric acid. The latter should be gotten rid of entirely in this way but we still have the excess of manganese chloride in the filtrate. This must now be brought to a boil, a sufficient quantity of H_2O_2 added with an excess of strong ammonia (0.9 sp.gr.) The hydrogen peroxide must be of at least ten volumes strength and it was customary to use about 20cc for a precipitation. With a few more minutes more of stirring and heating there should be a black, flocculent precipitate which allows the solution to filter easily and quickly. If,

for any reason, such as weakness of peroxide or lack of ammonia, this black precipitate is not obtained, but instead a brownish, slow filtering one, manganese is sure to come out in the filtrate and cause much trouble when igniting the alkalies. The precipitate, moreover, should not be more bulky than can well be handled on a 9 cm filter paper. This may be easily regulated by changing the original amount of $MnCl_2$ solution. The precipitate must be washed quickly with about 100cc of hot water, but too much washing must be avoided as this changes the character of the precipitate. The filtrate is then evaporated to dryness, the residue is ignited and the alkalies are weighed as chlorides.

It might be stated, before going further, that the method has been used by Professor Parr in Qualitative work with excellent results.

In these experiments it was found

that the manganese chloride was somewhat impure and it was necessary to subtract a rather high blank from all the results. Difficulty was also experienced with the hydrogen peroxide, there being practically none found in the American market which could be obtained free from sulphates and phosphates. As both of these would be detrimental when it is attempted to burn the alkalies as chlorides, a method for purification had to be sought. The easiest and simplest found was the distillation of the peroxide under reduced pressure, the vacuum obtained by a filter pump being sufficient for the purpose. The distillate is free from contamination and retains its pristine strength, but the addition of a little hydrochloric acid is necessary for preservation. Attempts were made to form the hydrogen peroxide from sodium peroxide and dilute sulphuric acid but proved unsuccessful because it was impossible to lessen the heat of the reaction which ensued during the

process which we employed. The distillate was always too weak.

The following results were obtained by using known solutions of the alkalies. Without using magnesia for separation we added 5 cc of an 8 o/o solution of Manganese chloride. These amounts were maintained all the way through.

Amt of NaCl taken	Found wt NaCl	Blank for impur $MnCl_2$	Actual wt NaCl	Loss	Percent. Loss
.0952	.0881	.0050	.0821	.0131	13.7
"	.0956	"	.0906	.0048	5.0
"	.0910	"	.0860	.0092	9.6
"	.0883	"	.0823	.0129	13.6
"	.0882	"	.0822	.0130	13.7
"	.0958	"	.0908	.0044	4.9
"	.0987	"	.0937	.0015	1.5
"	.0934	"	.0884	.0068	7.1
"	.0969	"	.0919	.0033	3.5
"	.0994	"	.0944	.0006	.6
"	.0835[+]	"	.0785	.0177	18.6

[+] In this sample the manganese phosphate precipitate was allowed to stand overnight and the result affirms Jolys

statement that this precipitate will take up alkalies. If the filtration and washing are carried out quickly, as directed above, no such difficulty is experienced. These results tabulated above are all low, and with the exception of perhaps three, are too low to be of value for analytical purposes. The same thing* will be noticed with the KCl.

Amt of KCl taken	Found wt KCl	Blank for impure reagent	Actual wt KCl	Loss	Percent Loss.
.1100	.1041	0050	.0991	.0109	9.99
″	.1081	″	.1031	.0069	6.28
″	.1136	″	.1086	.0014	1.28
″	.1072	″	.1022	.0078	7.07
″	.1081	″	.1031	.0069	6.28
″	.1041	″	.0991	.0109	9.99
″	.1058	″	.1008	.0092	8.33
″	.1034	″	.0984	.0116	10.05
″	.1155	″	.1105	+.0005	.44
″	.1101	″	.1051	.0049	.43
″	.1052	″	.1002	.0092	8.33
″	.1153	″	.1103	+.0003	.27
″	1075†	″	.1025	.0075	6.81
″	.1113‡	″	.1063	.0037	3.33
″	.1067T	″	.1017	.0083	7.54
″	.1098‡	″	.1048	0052	4.72

+ These two samples were washed with 100cc of water while ++ the other two were washed with double the amount. These four results seem to show that the alkalies are but loosely held and could be washed out if much washing could be employed. In order to locate the loss definitely, two rough experiments were made, in which a strong solution of the alkalies was treated with 50cc of a manganese chloride solution. The latter was precipitated in the usual manner with the peroxide and, after washing well, the precipitate was dissolved and then reprecipitated. The filtrate here contained alkalies in the following amounts.- (a) .2019 grams (b) .2218 grams. While these results are not quantitatively accurate they show two important facts. First, that the manganese precipitate is the offender in the retention of the alkalies and secondly, that the precipitate can be made to give up the most if not all of the retained alkalies. Washing alone will not bring this about because the wash water will gradually cause a change in the

character of the precipitate, which becomes smaller in bulk, brownish in colour and runs easily through the filter. Thus too much washing must be avoided.

The following determinations were made with reprecipitation of the manganese dioxide. The process was followed as usual but after washing the manganese precipitate well it was dissolved in a few cubic centimetres of strong hydrochloric acid. If neccessary, the addition of a few drops of hydrogen peroxide will greatly hasten the solution. The solution must be well boiled, about 20 cc of the peroxide added again and the excess of strong ammonia. The manganese dioxide is in this way thrown down again. After quickly washing this filtrate is added to the other. The results show that as far as chlorides alone are concerned the reprecipitation method is accurate. With sulphates the matter seems more difficult for some manganese usually appears in the alkali residue. If this is the case the latter do not ignite well but easily fuse to a dirty brown mass.

Amt of NaCl taken	Found wt NaCl.	Blank for impurities	Actual wt NaCl	Diff.	Percent.
.0952	.1000	.0050	.0950	-.0002	0.20
"	.0990	.0050	.0940	-.0012	1.26
.3808	.3823	.0050	.3793	-.0025	0.65
.4760	.4757	.0050	.4707	-.0053	1.12
KCl	KCl		KCl	KCl	
.1100	.1152	.0050	.1102	+.0002	0.18
"	.1173	.0050	.1123	+.0023	2.00
.4400	.4502+	.0050	.4452	+.0052	1.18
.5500	.5600+	.0050	.5550	+.0050	0.90
Na_2SO_4	Na_2SO_4		Na_2SO_4	Na_2SO_4	
.1296	.1332	.0050	.1282	-.0014	1.00
.2592	.2682	.0050	.2632	+.0040	1.58

+ These samples contained trace of manganese.

Attempts were also made to test the effects of suspended substances in the solution before precipitation. It was thought that if Aluminium hydroxide or calcium carbonate were suspended in the solution the alkalies would not be retained in the manganese dioxide. The method of procedure was the same as before except that to the filtrate from the manganese phosphate precipitate a little of the above mentioned substances were added in suspension.

Amt of NaCl + KCl taken	Found wt NaCl + KCl	Blank	Actual wt of NaCl + KCl	Loss	Percent Loss.
	Aluminium hydroxide used.				
.0821	.0797	.0050	.0747	.0074	9.02
"	0835	"	.0785	.0036	4.39
KCl + Na_2SO_4	KCl + Na_2SO_4		KCl + Na_2SO_4		
.0959	.0940	"	.0890	.0069	7.18
"	.0832	"	.0782	.0177	18.40
	Calcium carbonate used				
KCl + NaCl	KCl + NaCl		KCl + NaCl		
.0821	.0876	"	.0826	+.0005	0.60
"	.0860	"	.0810	.0011	1.33

N. The last two samples contained traces of Mn.

These results are for the most part low but seem to indicate that the method might be much improved along these lines. The time was, however, unfortunately too short to go farther into the matter.

In conclusion it may be stated that the method is shorter than some of the others now in use and has the advantage that the alkalies may be

determined from the same residue of the the boiler water as the rest of the bases sought after. When the manganese precipitate is dissolved and reprecipitated it is certainly as accurate as the others. There is difficulty experienced sometimes in getting the alkalies free from manganese but care in procedure will overcome this. Another hindrance lies in the fact that in some cases, as the process is carried out here, there is a possibility that the alkalies are finally weighed, not entirely as chlorides ~~but~~ in some part as sulphates. Judging, however, from the run of boiler waters analysed here, this condition does not often exist. As has been mentioned above, there are possibilities in doing away with the re-precipitation through the use of suspended materials and when this is accomplished the method will certainly have decided advantages as regards saving of time and accuracy.

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